EERC
Energy & Environmental Research Center
15 North 23rd Street, Stop 9018 • Grand Forks, ND 58202-9018 • P. 701.777.5000 • F. 701.777.5181
www.undeerc.org

January 28, 2021

Ms. Karlene Fine
Executive Director
North Dakota Industrial Commission
State Capitol, 14th Floor
600 East Boulevard Avenue, Department 405
Bismarck, ND 58505-0840

Dear Ms. Fine:

Subject: Quarterly Project Status Report Entitled "Low-Pressure Electrolytic Ammonia Production"; Contract No. R-036-45; EERC Fund 23228

Attached is a copy of the subject project status report for the period of October 1 through December 31, 2020.

If you have any questions, please contact me by phone at (701) 777-2982 or by e-mail at taulich@undeerc.org.

Sincerely,

DocuSigned by:
Ted Aulich
89B1B8E4D0E7430...

Ted R. Aulich
Principal Process Chemist
Fuels and Chemicals

TRA/kal

Attachment

c/att: Andrea Holl Pfennig, North Dakota Industrial Commission

LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION

Quarterly Project Status Report

(for the period of October 1, 2020, through December 31, 2020)

Prepared for:

Karlene Fine

North Dakota Industrial Commission
State Capitol, 14th Floor
600 East Boulevard Avenue, Department 405
Bismarck, ND 58505-0840

Contract No. R-036-45

Prepared by:

Ted R. Aulich

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

January 2021

EERC DISCLAIMER

LEGAL NOTICE This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by the U.S. Department of Energy (DOE) National Energy Technology Laboratory. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

ACKNOWLEDGMENT

This material is based upon work supported by the DOE National Energy Technology Laboratory under Award No. DE-EE0008324.

DOE DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

NDIC DISCLAIMER

This report was prepared by the Energy & Environmental Research Center (EERC) pursuant to an agreement partially funded by the Industrial Commission of North Dakota, and neither the EERC nor any of its subcontractors nor the North Dakota Industrial Commission nor any person acting on behalf of either:

(A) Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

(B) Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the North Dakota Industrial Commission. The views and opinions of authors expressed herein do not necessarily state or reflect those of the North Dakota Industrial Commission.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION
Quarterly Project Status Report
October 1 – December 31, 2020

EXECUTIVE SUMMARY

This quarterly report summarizes October–December 2020 progress made toward achieving milestones and objectives of the low-pressure electrolytic ammonia (LPEA) project under way at the University of North Dakota (UND) Energy & Environmental Research Center (EERC). Partners on the 3-year (June 2018 – July 2021) project include North Dakota State University (NDSU), Nel Hydrogen (formerly Proton OnSite), and the North Dakota Industrial Commission (NDIC). The project goal is to demonstrate an ammonia production energy reduction of at least 16% by replacing state-of-the-art (2018) high-pressure Haber–Bosch (HB)-based ammonia synthesis with the EERC-developed LPEA process. Achieving this energy reduction goal requires improving the proton conductivity, gas impermeability, and durability of the EERC–NDSU-developed polymer–inorganic composite (PIC) proton exchange membrane, a critical LPEA process component capable of high proton conductivity at 300°C. Key accomplishments of the October–December 2020 quarter include the following:

- Establishing an easily replicable and reliable protocol for using the recently procured “ProboStat” instrument to accurately measure proton conductivity of PIC membranes and electrolyte disks over a temperature range of 160° to 450°C.
- Producing a PIC electrolyte disk with a measured proton conductivity of 8×10^{-2} siemens/cm (S/cm) at 300°C, surpassing the project target of 10^{-2} S/cm by almost an order of magnitude.

The EERC holds an unwavering commitment to the health and well-being of its employees, partners and clients, and the global community. As such, precautionary measures have been implemented in response to Covid-19. Staff continue to carry out project-related activities remotely, and personnel supporting essential on-site laboratory and testing activities are proceeding under firm safety guidelines. Travel has been minimized, and protective measures are being undertaken for those who are required to travel. At this time, work conducted by EERC employees is progressing with minimal schedule disruption. Challenges posed by economic variability will be met with open discussion between the EERC, the U.S. Department of Energy (DOE) Project Manager, and other partners to identify solutions. The EERC is monitoring developments across the nation and abroad to minimize risks, achieve project goals, and ensure the success of our partners and clients.

LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION
Quarterly Project Status Report
October 1 – December 31, 2020

PROJECT GOALS/OBJECTIVES

The project goal is to demonstrate an ammonia production energy reduction of 16% by replacing state-of-the-art (2018) high-pressure HB-based ammonia synthesis with the EERC-developed LPEA process, as shown in Figure 1. To achieve the 16% production energy reduction target will require improving the LPEA process, which will require improving the PIC proton exchange membrane (PEM) on which the LPEA electrochemical cell is based. As a result, the

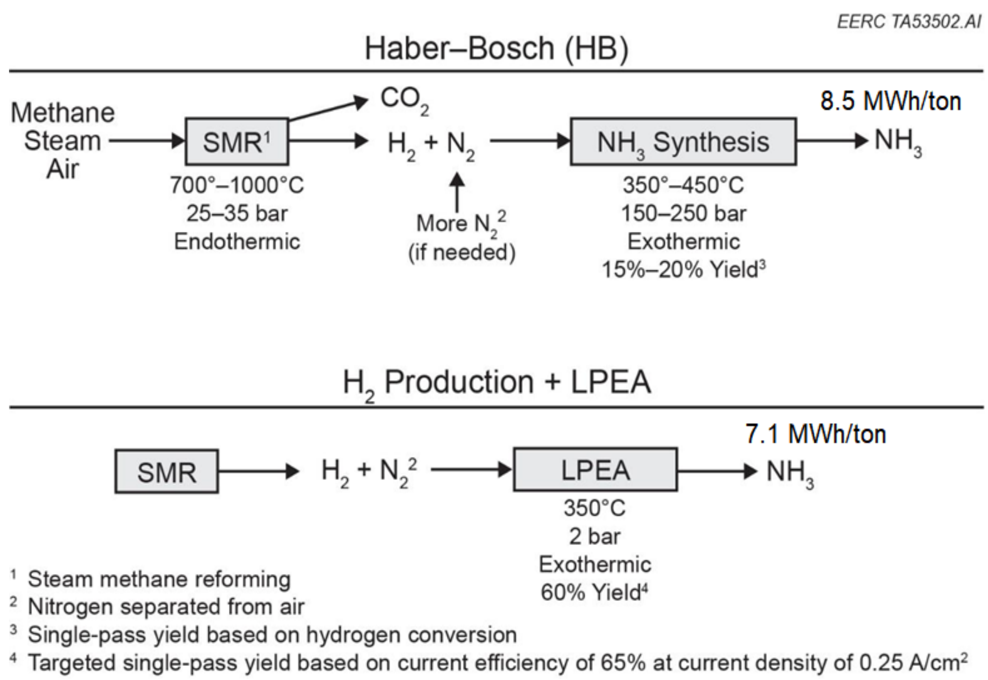


Figure 1. State-of-the-art (2018) HB versus LPEA-based NH_3 production.

proposed project is focused on improving the performance and durability of the PIC membrane, with the objective of producing a membrane that exhibits the following properties:

- Proton conductivity of $\geq 10^{-2}$ siemens/centimeter (S/cm) and gas permeability of <2% at a minimum temperature of 300°C.
- Ability to sustain 10^{-2} S/cm proton conductivity for at least 1000 hours (h).
- Mechanical strength (at 300°C) comparable to that of a commercial proton exchange-based electrolyzer membrane.

- As measured in a membrane–electrode assembly (MEA) at a minimum temperature of 300°C, current efficiency of ≥65% for NH_3 formation at a current density of ≥0.25 amps/cm^2 (A/cm^2), NH_3 production energy efficiency of ≥65%, and ≤0.3% performance degradation per 1000 h of operation.

BACKGROUND

In support of DOE Energy Efficiency and Renewable Energy (EERE) Advanced Manufacturing Office (AMO) goals to reduce life cycle energy consumption of manufactured goods and more cost-effectively use hydrogen in manufacturing processes, this project is focused on optimizing and demonstrating the improved efficiency (versus HB ammonia production) of the EERC-developed LPEA production process. Because it does not require the high pressure and high recycle rate (because of low single-pass ammonia yield) of the HB process, LPEA offers the potential for significant reduction in both energy consumption and cost. Partners on the proposed project are NDSU, Nel Hydrogen (Nel) (formerly Proton OnSite), the UND Chemistry, and NDIC. The LPEA process is based on an innovative EERC-developed PIC high-temperature PEM. The process operates at ambient pressure and a temperature of 300°C and uses inputs of hydrogen, nitrogen, and electricity to make ammonia. The EERC demonstrated LPEA process viability in ammonia formation tests conducted using a 0.2-watt electrochemical cell built around an early-stage PIC membrane.

To meet the above-listed membrane performance and durability specifications, the project initially targeted fabrication—via a "coelectrospinning" technique—of a PIC membrane comprising "core–shell" inorganic proton conductor–polybenzimidazole (IPC–PBI) proton-conducting nanofibers contained within and aligned perpendicularly to the plane of a PBI matrix/membrane, as shown in Figure 2. Because each fiber core would comprise a chain of IPC particles in contiguous contact with one another throughout the chain length, each fiber would essentially function as a high-efficiency proton transport conduit running straight through the membrane. However, during Budget Period 1 (BP1) of the project, an alternative IPC was identified that offered significantly improved proton conductivity, stability, and durability—at 300°C—than the originally proposed IPC. Because this new IPC (IPC2) encompasses chemical and physical properties not amenable to coelectrospinning with PBI to yield core–shell nanofibers, new methods for IPC2 deployment in PBI matrix are being pursued. Primary focus is on film-casting (also called solution-casting) membranes using a colloidal suspension of optimally sized IPC2 particles in a solution comprising PBI dissolved in dimethylacetamide (DMAc). Secondary focus is on fabricating thin-disk electrolytes using a high-temperature press.

Following fabrication of a PIC membrane/disk that meets performance and durability specifications, the membrane—along with selected anode and cathode catalysts—will be used to construct experimental MEAs. MEAs will be incorporated into LPEA unit cells that will be evaluated based on NH_3 formation efficiency and durability, with the objective of identifying an optimal MEA configuration. The optimal MEA configuration will be used as the basis for building a stack of several LPEA unit cells that will compose an LPEA system capable of producing at least 100 grams/day (g/d) of NH_3. The 100-g/d LPEA system will undergo optimization and then be used to demonstrate NH_3 synthesis (from H_2) at the LPEA target

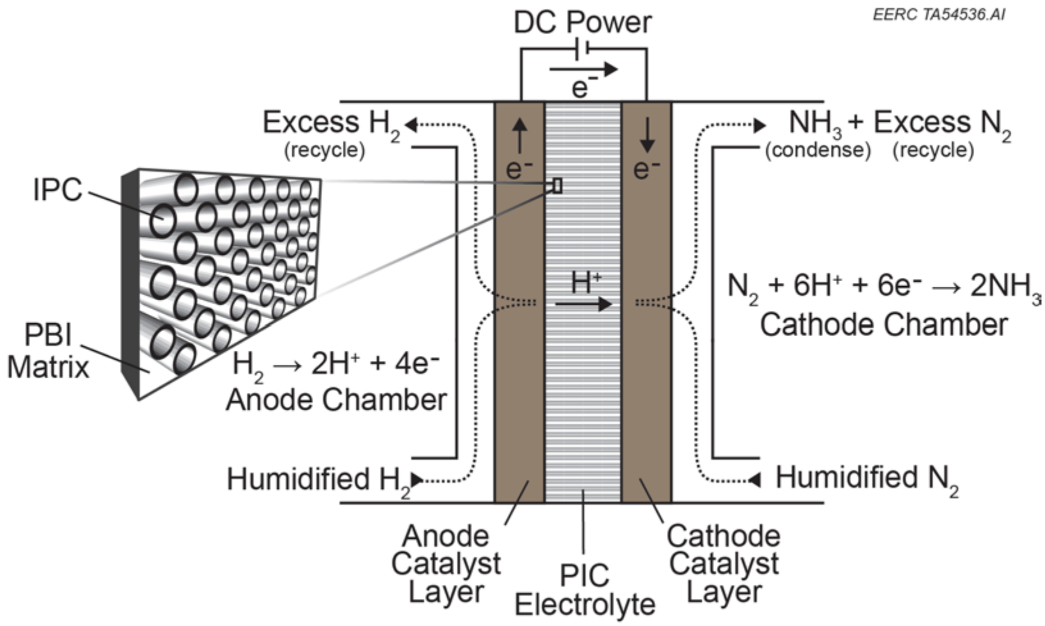


Figure 2. LPEA process.

production energy input requirement of 0.8 megawatt hours (MWh/ton), which would translate to a total (H_2 production plus NH_3 synthesis) LPEA-based NH_3 production energy input requirement of 7.1 MWh/ton, the project goal. LPEA system operation and performance data will be used to perform a techno-economic evaluation of the LPEA-based NH_3 production process.

ACCOMPLISHMENTS

Key accomplishments during the October–December 2020 reporting period include the following:

- Establishing an easily replicable and reliable protocol for using the recently procured “ProboStat” instrument to accurately measure proton conductivity of PIC membranes and electrolyte disks over a temperature range of 160° to 450°C.

- Producing a PIC electrolyte disk with a measured proton conductivity of 8×10^{-2} S/cm at 300°C, surpassing the project target of 10^{-2} S/cm by almost an order of magnitude.

PROGRESS AND STATUS

Task 1 – Project Management

As shown in Table 1, a 6-month no-cost project extension was formally requested on January 7, 2021. The need for this extension derives from 1) a tentative BP2 start while awaiting official approval of BP2 funding, 2) remote-work directives issued in response to Covid-19 spread concerns (limiting laboratory activities), and 3) major delay in procurement of an instrument (ProboStat) needed for accurate measurement of PIC membrane proton conductivity. Because inability to conduct LPEA project work resulted in conservation of LPEA project funding, sufficient budget is available to complete the project.

Table 1. Task Schedule – BP2

Task No.	Task Description	Task Completion Date: Original Planned	Revised Planned	% Complete	Task Progress Notes
1	Project Management	June 2021	Dec. 2021	70	6-month no-cost extension requested on 7 Jan. 2021
3	Optimize IPC and PIC membrane performance and durability	Dec. 2020	June 2021	65	New instrument for membrane assessment now available
5	Screen cathode catalysts, fabricate MEAs, deploy MEAs in unit cell for LPEA process optimization	Dec. 2020	June 2021	50	Catalysts screened; MEA and unit cell work ongoing
6	Design, fabricate, and optimize 100-g/d LPEA system; acquire data for techno-economic analysis	March 2021	Sept. 2021		Task work initiated in January 2021
7	Conduct techno-economic analysis	June 2021	Dec. 2021		Not started

Task 3 – Optimize IPC and PIC Membrane Performance and Durability

Evaluation of planetary ball milling methods for IPC2 particle-size reduction continued. A 60-g sample of IPC2 was sent to a commercial planetary mill manufacturer for test grinding, with the objective of ascertaining whether the mill can achieve 1) an average IPC2 particle size of 100–200 nm and 2) a narrow particle-size distribution. Work also continued on development of methods for producing thin, densified, and possibly “prestressed” PIC electrolyte disks via hot-pressing IPC2 or an alternative IPC2 formulation with enhanced proton conductivity (referred to as “IPC2-A2”) in combination with PBI or one of two identified inorganic binders.

Figure 3 compares FTIR spectra of IPC2 and IPC2-A2. The region of 2600–3600 cm^{-1} indicates the presence of OH groups in the IPC2-A2 material, theorized to be responsible for the previously reported (July–Sept 2020) 50% higher proton conductivity of IPC2-A2 versus IPC2. PIC electrolyte disk mixtures undergoing evaluation include the following:

- IPC2 and PBI binder
- IPC2 and ceramic/inorganic binders
- IPC2-A2 and PBI binder
- IPC2-A2 and ceramic/inorganic binders

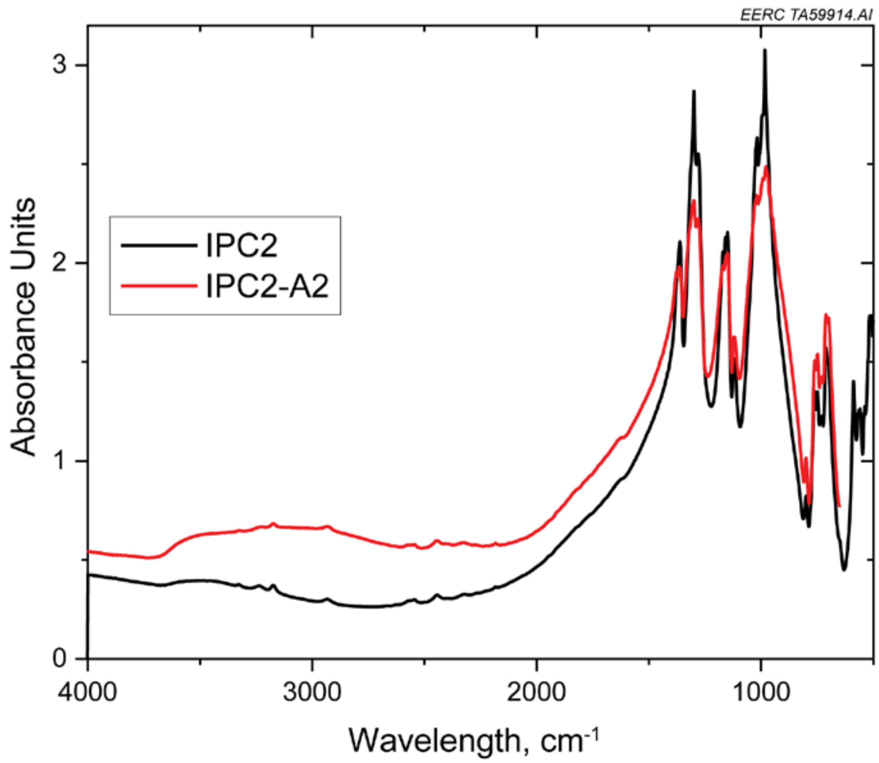


Figure 3. FTIR (Fourier transform infrared) spectra of IPC2 and IPC2-A2.

As described in prior quarterly reports, surface oxidation of the sample holder used for measuring membrane proton conductivity at 300°C was identified as the source of inaccurate conductivity data. A “ProboStat™” instrument designed by the University of Oslo specifically for measuring electrical properties of materials at high temperatures was procured. After establishing a protocol for using the ProboStat to measure proton conductivity over a temperature range of 160°–450°C, a recently fabricated PIC electrolyte disk comprising 97% IPC2–3% PBI was evaluated. The disk exhibited a 300°C proton conductivity of 8×10^{-2} S/cm, almost an order of magnitude higher than the primary project success criterion of 10^{-2} S/cm.

Task 5 – Catalyst Screening and MEA/Unit Cell Development and Optimization

No catalyst screening work was conducted during the reporting quarter. A set of MEAs comprising membrane (75% IPC2–25% PBI), niobium nitride cathode, and platinum anode was fabricated by Nel using a specially developed airbrushing technique. The MEAs are awaiting evaluation.

Task 6 – Design, Fabrication, and Operation of 100-g/d LPEA System

No activity this quarter.

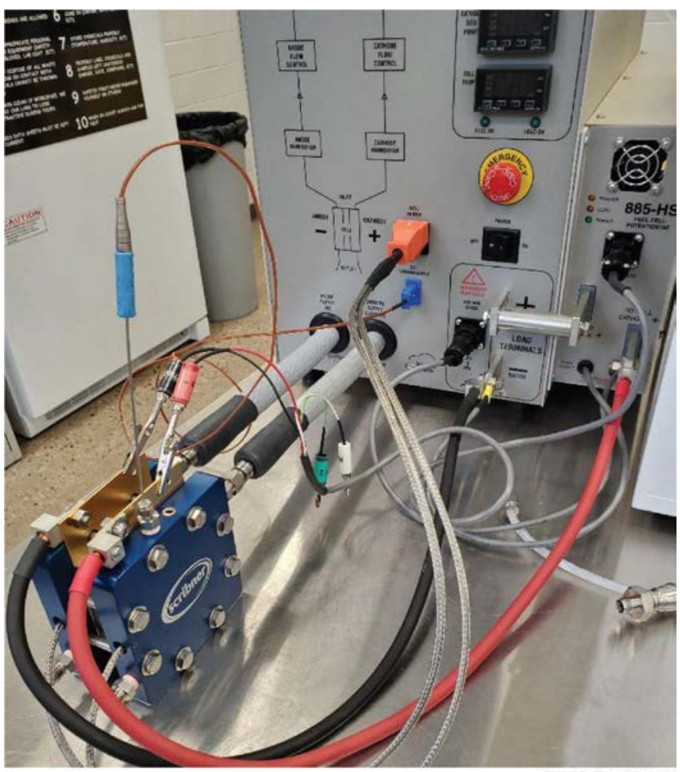
Task 7 – Techno-Economic Analysis

No activity this quarter.

PLANS FOR NEXT QUARTER

Task 3 – Optimize IPC and PIC Membrane Performance and Durability

Optimization of methods for fabrication, evaluation, and optimization of PIC membranes and PIC thin disk electrolytes will continue. Analytical efforts will focus on application of the ProboStat to measuring—for each membrane/electrolyte sample—the critical electrochemical properties (at 300°C) of proton conductivity, gas permeability/crossover, and thermal decomposition. To help expedite PIC membrane fabrication technique optimization, NDSU recently procured a fuel cell test stand (Figure 4) for preliminary evaluation of NDSU-produced membranes prior to shipping them 80 miles north to the EERC. While the NDSU test stand is currently limited to a maximum operational temperature of 180°C, options for increasing the operational temperature to 300°C are being explored.



EERC TA59915.AI

Figure 4. Scribner® 850e Multi-Range Fuel Cell Test System connected to unit cell.

Task 5 – Catalyst Screening and MEA/Unit Cell Development and Optimization

Additional MEAs will be fabricated and evaluated based on ammonia synthesis rate and current efficiency.

Task 6 – Design, Fabrication, and Operation of 100-g/d LPEA System

Initiate design of 100-g/d system.

Task 7 – Techno-Economic Analysis

Develop strategy/deployment scenario for economically competitive initial entry of LPEA into the commercial ammonia industry.

PRODUCTS

None.

IMPACTS

Impact on Technology Transfer and Commercialization Status

No commercialization impacts, progress, issues, or concerns to report during this quarter.

Dollar Amount of Award Budget Being Spent in Foreign Country(ies)

No spending of any project funds in any foreign countries has occurred or is planned.

CHANGES/PROBLEMS

The EERC is operational and open for business. Personnel that are not essential for on-site operations have transitioned to working from home. Essential project, laboratory, and field-based activities are proceeding with the incorporation of the Centers for Disease Control and Prevention, the state of North Dakota, and UND guidelines associated with COVID-19, and mitigation measures have been implemented. In collaboration with project partners, the EERC is continually assessing potential impacts to project activities resulting from COVID-19 and/or the U.S. economic situation. As discussed earlier, the project is about 6 months behind schedule.

Scope Issues, Risks, and Mitigation Strategies

None.

Actual or Anticipated Problems or Delays and Corrective Actions or Plans to Resolve

To accommodate the approximate 6-month progress delay, a 6-month no-cost extension was requested on 7 January 2021.

Changes That Have a Significant Impact on Expenditures

None.

RECIPIENT AND PRINCIPAL INVESTIGATOR DISCLOSURES

None.

CONFLICTS OF INTEREST WITHIN PROJECT TEAM

None.

PARTNERS AND FINANCIAL INFORMATION

This project is sponsored by NDIC, DOE, UND Chemistry, NDSU, and Proton. Table 2 shows the total budget of $3,164,010 for this project and expenses through the reporting period.

Table 2. Project-to-Date Financial Report at December 31, 2020

Funding Source	Budget	Current Reporting Period Expenses	Cumulative Expenses as of 12/31/20	Remaining Balance
DOE	$2,497,983	$155,600	$1,836,406	$661,577
UND Chemistry – In Kind	$69,027	$762	$69,027	$0
NDIC	$437,000	$18,510	$334,494	$102,506
NDSU – In Kind	$120,000	$0	$120,000	$0
Proton – In Kind	$40,000	$1,544	$16,946	$23,054
Total	**$3,164,010**	**$176,416**	**$2,376,873**	**$787,137**